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ELECTROPHOTOGRAPHIC RECORDING PAPER FOR USE IN THE PREPARATION OF A PLANOGRAPHIC PLATE
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FIG. 1
PRIOR ART

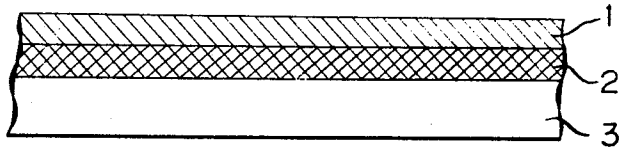


FIG. 2
PRIOR ART

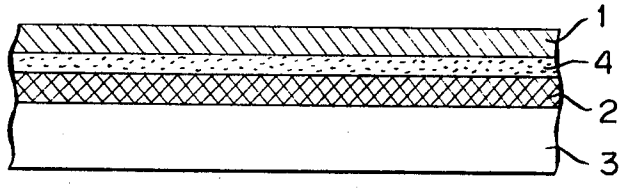
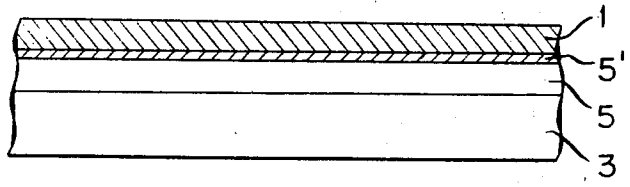


FIG. 3



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ELECTROPHOTOGRAPHIC RECORDING PAPER FOR USE IN THE PREPARATION OF A PLANOGRAPHIC PLATE

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Continuation-in-part of abandoned application Ser. No. 714,505, Mar. 20, 1968. This application Aug. 31, 1970, Ser. No. 68,460

Int. Cl. G03g 5/02, 13/22

U.S. Cl. 96—1.5 6 Claims

ABSTRACT OF THE DISCLOSURE

The invention relates to an article of manufacture, a novel electrophotographic sheet material adapted for use in the preparation of a planographic plate, comprising a support sheet and a layer or sheet of photoconductive material supported thereby, the two materials having an intermediate layer or sheet positioned between them comprising a water- and alcohol-soluble resin and which has the additional property of becoming coagulated or flocculated and rendered water-insoluble upon contact with an acid solution containing metal ions having a valence of 2 or more.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our copending application Ser. No. 714,505, filed Mar. 20, 1968, now abandoned.

BACKGROUND OF THE INVENTION

(a) Field of the invention

The field of this invention relates to improved electrophotographic sheet material, particularly recording paper adapted for use in the preparation of a planographic plate, said recording paper having, between a support paper sheet and a photoconductive layer formed thereon, an intermediate layer consisting of a resin which is characteristically soluble in both water and alcohol, said layer being such that it becomes locally insoluble in water in the process of making a printing plate and also in the process of printing.

(b) Description of the prior art

A planographic plate, in general, which is obtained by the application of the electrophotographic techniques has been prepared by the procedure in which a copied image is first formed on the photoconductive layer of an electrophotographic recording paper by using known electrophotographic copying techniques, and thereafter making the nonimage areas of the resulting copying paper hydrophilic, using a treatment solution designed for printing. An electrophotographic recording paper for use in the preparation of a planographic plate according to the above-described procedure has critical requirements such as being suitable for the preparation of a planographic plate and being suitable for the printing. An electrophotographic recording paper which lacks these properties will not produce a satisfactory planographic plate. Another critical and practical requirement is durability and resistance to wear accruing from continuous printing of a large number of paper sheets.

As the conventional electrophotographic recording papers for use in the preparation of such printing plates as described above, those having the structures illustrated in FIGS. 1 and 2 are known.

FIG. 1 shows an enlarged fragmentary, cross section of an electrophotographic recording paper, the structure of which consists of a support paper sheet 3, an intermediate layer 2 which is comprised of a hydrophilic substance of high molecular weight such as polyvinyl alcohol, carboxymethyl cellulose, gelatin or casein and which is formed directly on one surface of said support sheet, and a photoconductive layer 1 which is provided on the upper surface of said intermediate layer.

FIG. 2 shows an enlarged fragmentary cross section of another type of electrophotographic recording paper, which has a structure such that a layer 4 of a synthetic resin consisting of a urea resin or a melamine resin, each of which contains either an acid or a salt, is provided between the photoconductive layer 1 and the intermediate layer 2 of an electrophotographic recording paper.

While a recording paper having the structure as illustrated in FIG. 1 permits a clear copied image suitable for printing to be formed thereon, it is to be noted that in case this recording paper is applied as a planographic plate to a planographic press, in actual operation, there is the disadvantage that the treatment solution and the fountain solution which are applied onto the printing surface of the plate during the plate-making and printing processes for the purpose of making the nonimage areas of the plate hydrophilic or oil-repellent will infiltrate through the porous photoconductive layer 1 onto the intermediate layer 2 to dampen the latter and eventually dissolve this layer. As a result, the photoconductive layer 1 will be detached in whole or in part from the surface of the supporting sheet. A printing plate in such a state is not suitable for use in the making of a great number of prints, and for this reason, conventional electrophotographic recording papers having the structure of FIG. 1 are unsatisfactory with respect to their resistance to wear.

An electrophotographic recording paper having a structure as mentioned in FIG. 2, on the other hand, has increased durability characteristics by reason of layer 4 composed of a synthetic resin which becomes insoluble in water as a result of the heat treatment to which the recording paper is subjected. Therefore, the trouble of fragility which occurs in those recording papers having the structure of FIG. 1 is overcome. For this reason, the electrophotographic recording paper having the structure of FIG. 2 has a satisfactory resistance to wear during long term usage. This latter recording paper, however, has a number of critical drawbacks in that (1) it requires a long time to manufacture and the cost of its manufacture is high; and moreover (2) this recording paper requires a complicated and elaborate control and operation in the process of forming the intermediate layer, the layer of synthetic resin and the photoconductive layer on the support sheet, so that it is difficult to obtain products having uniform properties. In addition, this recording paper of the prior art has a further disadvantage (3) that the very high electric resistance of its intermediate layer leads to an undesirable, marked reduction in the photosensitivity of the photoconductivve layer formed on said intermediate layer.

SUMMARY OF THE INVENTION

The present invention overcomes the disadvantages of the prior art through the use of the novel combination of the intermediate layer with and interposed between the photoconductive layer and the support sheet.

Mechanically the novel article of manufacture can be made by any sequence of steps which brings the elements into their correct relative positions. Practically, it is preferred to start with the support sheet material, which can be any of the conventional support sheet materials used in the art for this purpose and place upon it the successive layers as will be described in detail below.

More specifically, the object of the present invention

includes the improved article which overcomes the disadvantages of the prior art conventional electrophotographic recording papers for use in the preparation of planographic plates, by the provision of the novel intermediate layer which consists of a class of materials possessing the critical properties heretofore mentioned and hereinafter described in detail.

As will be understood from the following descriptions, the present invention contemplates the provision of a novel electrophotographic recording sheet material for use in making planographic plates that are unobviously durable and hence have particular advantage in use for continuous printing runs. The novel sheet material is characterized in that the conversion to a printing plate is simplified in contrast to the manufacture of prior sheets with special durability properties, and can be accomplished by treatment of the sensitized sheet with a treating solution containing metal ions having a valence of 2 or more and an acid, and further that it is subjected during the printing operation while being moistened with a fountain solution having a similar composition to that of said treatment solution.

For purposes of side-by-side comparison in more detail with the invention, the foregoing description of the prior art products represented by FIG. 1 and FIG. 2 is reviewed briefly as follows:

FIG. 1 shows an enlarged fragmentary cross section of one example of the conventional electrophotographic recording papers for use in the preparation of planographic plates, wherein **1** represents a photoconductive layer, **2** an intermediate layer, and **3** a support sheet.

FIG. 2 shows an enlarged fragmentary cross section of one example of the conventional electrophotographic recording papers of another type designed for use in the preparation of planographic plates, wherein the recording paper is provided with a further layer **4** of a synthetic resin in addition to the structure mentioned in FIG. 1.

FIG. 3 shows an enlarged fragmentary cross section of one example of the article of this invention wherein **1** is the photoconductive layer, **5'** and **5** together represent the novel intermediate layer between the photoconductive layer **1** and the support sheet **3**. The intermediate layer is included in the novel aspect of this invention and is shown as composed of **5'** a water-insoluble film which is developed during the process of making the planographic printing plate and remains so during the process of printing. The chemical substance of the intermediate layer **5'–5** is substantially the same throughout its combined thickness, the differences and unobvious advantages of the two elements of this intermediate layer will be described below.

The critical property of the intermediate layer is that, prior to plate-making, it is selected from those substances which have the property of becoming hardened, i.e., coagulated or flocculated upon being contacted with the treating solution described above. This hardening effect can be superficial as **5'** or can extend through the entire layer. Thus, after a copied image is formed by performing the known techniques, the article of this invention is treated with a treatment solution containing an acid and metal ions having a valence of 2 or more, there is formed upon the intermediate layer a water-insoluble film as shown at **5'** in FIG. 3 by penetration of the treating solution to reactive contact with the intermediate layer. This hardening treatment imparts to the plate an imperviousness to the aqueous solutions used in plate-making and printing, the coagulated or flocculated film **5'** providing a positive barrier against the infiltration of such aqueous solutions and consequently eliminates a principal cause of the deterioration of the plate by distintegration.

As the resins which can be applied to the present invention in the formation of intermediate layers, the employment of partially saponified resins which are obtained by saponificating 60 to 95 percent of a polymer selected from the group consisting of polymethylacrylate, polyethylacrylate, polymethylmethacrylate, polyethylmethacrylate, vinyl methyl ether-maleic anhydride copolymer and styrene-acrylic acid copolymer with sodium hydroxide or ammonium hydroxide are suitable.

The fact that these partically saponified resins are soluble characteristically in solvents such as water and alcohol affords the advantage that the operation of forming the intermediate layers by applying the resin as a solution onto the supports is facilitated and also that the applied solution can be dried easily to form the layer. The provision of such an intermediate layer as described above not only prevents the infiltration and diffusion of the organic solvent contained in the solution intended for forming a photoconductive layer into the support sheet at the time the photoconductive layer is formed on the surface of said intermediate layer by applying the solution thereonto and thus facilitates the formation of the photoconductive layer on the surface of the intermediate layer, but also it contributes to the enhancement of the adherency of the treatment solution onto the nonimage areas in the process of making a printing plate as well as in the process of printing. Accordingly, the present invention not only allows the electrophotographic recording paper to be manufactured easily but also it affords facile production of products of uniform properties. It is needless to say that in the present invention the employment of a support paper which has been sized beforehand at the time the paper is made to prevent the aforesaid infiltration of the solvent thereinto will bring about a further effective result. Such sizing agents include, for example, rosin, polyvinyl alcohol, carboxymethyl cellulose, urea resin, melamine resin and starch.

As the materials for the formation of photoconductive layers which are used in the present invention, any one of the known photoconductive substances and the known sensitizing dyestuffs which have been utilized in the conventional electrophotographic recording papers can be employed. Of all these photoconductive substances, however, photoconductive zinc oxide is preferred. As for the resins which are employed in the formation of or for the binding of the photoconductive layers containing such photoconductive substances and dyestuffs, the employment of natural and synthetic resins is recommended. Such resins include, for example, silicone resin, acrylic resin, alkyd resin, modified alkyd resin and styrene-butadiene resin.

As for the sensitizing dyestuffs, for example, Rose Bengal (C.I. No. 45440), Rhodamine B (C.I. No. 45170), Methyl Violet (C.I. No. 42535), Methylene Blue FZ (C.I. No. 52015), Brilliant Green CX (C.I. No. 42040) and Acridine Yellow (C.I. No. 47005) etc., are suitable.

The planographic plate which is obtained from the electrophotographic recording paper of the present invention is based on the novel effect of the treatment solution for use in printing, i.e., an acid solution that contains metal ions having a valence of 2 or more. Such a treatment solution is most suitable for such planographic plates as having a photoconductive layer formed thereon. As the treatment solution for use in planographic plates which are obtained from electrophotographic recording papers, various kinds of solutions are known. As the treatment solution for the electrophotographic recording papers of the present invention having an intermediate layer consisting of any one of the aforesaid water-soluble resins, it has been found, as the result of a number of experiments, that the following treatment solutions are suitable.

More particularly, it has been found that those treatment solutions consisting substantially of an aqueous solution containing dissolved therein at least one acid selected from the group consisting of phosphoric acid and acetic acid, at least one phosphate selected from the group consisting of diammonium hydrogen phosphate and ammonium dihydrogen phosphate and at least one metal ion having a valence of 2 or more, said metal ion being intro-

duced into the solution in the form of salt such as zinc, nickel, calcium, magnesium, copper, barium, cadmium, lead and iron salts of hydrochloric acid, nitric acid and sulfuric acid, are most suitable. So long as a treatment solution as described above is used, there is no danger at all for a staining of prints with the printing ink, and thus an important unobvious effect is displayed in the printing of a large number of papers.

The thickness of the intermediate layer should be such that the establishment of effective electrostatic charge caused by exposure of the photoconductive layer is not impaired. Likewise the thickness of the photoconductive layer must be such as to permit establishment of reactive contact between the treatment solution and the intermediate layer during plate-making. These layer thicknesses are of the same order as the thicknesses of prior interlayers and photoconductive layers. As examples of thicknesses and thickness ranges suitable for the practice of this invention, a thickness of an intermediate layer to be formed onto a surface of a support is desirable in the range of 1μ–20μ, more preferably, in the range of 5μ–10μ. The thickness of a photoconductive layer to be formed on the upper surface of the aforesaid intermediate layer is desirably in the range of 5μ–30μ, more preferably, in the range of 10μ–30μ.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Onto one surface of a base paper having been sized beforehand so as to prevent the infiltration thereinto of the solvent, was applied a solution having the following composition to form an intermediate layer having a thickness of about 10μ:

Saponified polymethylacrylate (in which 80 percent of the polymer is saponified with sodium hydroxide): 5 gr.
Methanol: 95 gr.

After the same was dried, a solution having the following composition and intended for the formation of a photoconductive layer having a thickness of about 20μ was applied onto the upper surface of said intermediate layer which was formed already:

Silicone resin for use in painting: 30 gr.
Toluene: 80 gr.
Zinc oxide: 100 gr.
Sensitizing dyestuff (5 percent methanol solution): 2 cc.

The electrophotographic recording paper for use in planographic printing which was prepared in a manner described above was regulated of its moisture content under a condition of 65 percent RH for 12 hours. Then, the recording paper was provided with electrostatic negative charge by means of a corona discharge, then exposed to light through an original and was developed according to a known dry process electrophotographing technique. As a result, a clear copied image was obtained. In order to determine the copying ability of this recording paper, a duplicate was made on the recording paper of the present invention by the use of a test chart carrying more than 10 fine lines spaced at 1 mm. intervals and according to the electrophotographic technique. The result was that all of the copied fine lines were clearly recognized. This means that the recording paper of the present invention had a very good resolving power. Then, the aforesaid copied image was heat-fixed at 150° C. for 30 seconds, followed by making a nonimage area of the resulting recording paper hydrophilic by the application of the treatment solution of the following composition:

Aqueous solution of 40 percent nickel nitrate: 100 cc.
Aqueous solution of 20 percent; diammonium hydrogen phosphate: 100 cc.
Phosphoric acid: 10 cc.

A solution prepared by diluting the aforesaid treatment solution with water of an amount 6 times as much as that of said treatment solution was used as the fountain solution. Printing was conducted by the use of this fountain solution on a synchronism-type offset printing machine. The prints of a number of more than 7000 were noted to be invariably clear.

Example 2

Onto one surface of a size base paper was applied a solution intended for use in the formation of an intermediate layer and having the following composition:

Saponified polyethylmethacrylate (in which 95 percent of the polymer is saponified with ammonium hydroxide: 12 gr.
Ethanol: 88 gr.

After completely drying the same, an intermediate layer having a thickness of about 10μ was formed, then a solution having the following composition and intended for the formation of a photoconductive layer having a thickness of about 10μ was applied onto the upper surface of the intermediate layer formed and was dried.

Silicone resin for use in printing: 30 gr.
Toluene: 80 gr.
Zinc oxide: 200 gr.
Sensitizing dyestuff (5 percent methanol solution): 2 cc.

On the surface of the photoconducting layer of the electrophotographic recording paper thus obtained and for use in the preparation of planographic plates was formed an image by the same method as that of Example 1, viz, dry process electrophotographic technique. The developer adhering to the image areas of the copy was fixed by heat at 120° C. for 1 minute. Thereafter, the nonimage areas of the copy were made hydrophilic by the use of the treatment solution having the following composition:

Aqueous solution of 20 percent nickel sulfate: 60 cc.
Aqueous solution of 20 percent ammonium dihydrogen phosphate: 40 cc.
Phosphoric acid: 4 cc.

One part of this treatment solution was diluted with 4 parts of water and the resulting diluted solution was used as a fountain solution in the planographic printing which was performed on an ordinary offset printing machine using Morton rollers. A total of runs of more than 7000 prints invariably provided very clear copies.

Example 3

Electrophotographic recording papers for use in the preparation of planographic plates were prepared by using solutions for forming an intermediate layer and a photoconductive layer. The compositions of the solutions used are expressed in the following Table 1.

TABLE 1

Recording paper	Composition of intermediate layer	Composition of photoconductive layer
1	Saponified polyethylacrylate (in which 80% of the polymer is saponified with sodium hydroxide), 5 gr., methanol, 95 gr.	Same composition as that of Example 2.
2	Saponified vinyl methyl ether/maleic anhydride copolymer (in which 60% of the copolymer is saponified with sodium hydroxide), 5 gr., ethanol, 95 gr.	Do.
3	Saponified styrene/methylacrylate copolymer (in which 70% of the copolymer is saponified with ammonium hydroxide), 5 gr., methanol, 95 gr.	Do.

By means of a corona discharge, the coated dry photoconductive layer was provided with a negative electrostatic charge, then exposed and developed by the same electrophotographic method as that of the method described in Example 2.

Then, the nonimage areas of the copies were made hydrophilic by the use of the treatment solutions having compositions expressed in the following Table 2.

TABLE 2

Solution	Composition	Cc.
1	Aqueous solution of 10% calcium chloride	120
	Aqueous solution of 20% ammonium dihydrogen phosphate.	40
	Acetic acid	4
2	Aqueous solution of 10% barium nitrate	120
	Aqueous solution of 20% diammonium hydrogen phosphate.	40
	Phosphoric acid	4
3	Aqueous solution of 10% ferric sulfate	120
	Aqueous solution of 20% ammonium dihydrogen phosphate.	4
	Acetic acid	4

The fountain solutions were prepared by diluting the treatment solutions with water. And, the planographic printing was conducted by the use of this fountain solution on the same printing machine as that of Example 2.

The treatment solution **1** was applied to the above-described recording paper **1**, likewise the treatment solution **2** to the recording paper **2**, and the treatment solution **3** to the recording paper **3**, respectively. And, in either case, as in Example 2, there were obtainable copies of more than 7000 prints. Furthermore, in the case that calcium chloride, barium nitrate and nickel sulfate in the treatment solutions referred to in the respective examples were substituted by one of zinc chloride, magnesium chloride, copper nitrate, cadmium sulfate and lead sulfate, thereby obtained results were the same as those in the respective examples.

What is claimed is:

1. An electrophotographic recording sheet material for use in the preparation of planographic printing plates which comprises a support sheet, a photoconductive layer and an intermediate layer positioned between said support sheet and said photoconductive layer, said intermediate layer comprising a partially saponified resin selected from the group consisting of polymethylacrylate, polyethylacrylate, polymethylmethacrylate, polyethylmethacrylate, vinyl methyl ether-maleic anhydride copolymer and styrene-acrylic acid copolymer;

the degree of saponification of said resin being in the range of 60 and 95 percent, said photoconductive layer being of sufficient permeability to permit establishment of reactive contact between said intermediate layer and aqueous treatment solution applied to said photoconductive layer, said aqueous treatment solution containing dissolved therein at least one acid selected from the group consisting of phosphoric acid and acetic acid, at least one phosphate selected from the group consisting of diammonium hydrogen phosphate and ammonium dihydrogen phosphate and at least one metal ion having a valence of at least 2.

2. An electrophotographic recording sheet material of claim **1**, in which said partially saponified resin is obtained by saponifying 60 to 95 percent of a polymer selected from the group consisting of a polymethylacrylate, polyethylacrylate, polymethylmethacrylate, polyethylmethacrylate, vinyl methyl ether-maleic anhydride copolymer and styrene-acrylic acid copolymer with an alkaline compound selected from the group consisting of sodium hydroxide and ammonium hydroxide, and said photoconductive layer consisting essentially of a binding resin including dispersed

therein a photoconductive substance, said photoconductive layer being formed on the upper surface of said intermediate layer.

3. An electrophotographic recording paper according to claim **1**, wherein a thickness of said intermediate layer is in the range of from 1μ to 20μ.

4. An electrophotographic recording paper according to claim **1**, wherein a thickness of said photoconductive layer is in the range of from 5μ to 30μ.

5. An electrophotographic recording paper according to claim **1**, wherein said metal ion in the treatment solution is selected from the group consisting of zinc, nickel, calcium, magnesium, copper, barium, cadmium, lead and iron.

6. A process for preparing a planographic printing plate utilizing an electrophotographic sheet material which comprises a support sheet, a photoconductive layer and an intermediate layer positioned between said support sheet and said photoconductive layer, said intermediate layer consisting essentially of a partially saponified resin selected from the group consisting of polymethylacrylate, polyethylacrylate, polymethylmethacrylate, polyethylmethacrylate, vinyl methyl ether-maleic anhydride copolymer and styrene-acrylic acid copolymer, the degree of saponification of said resin being in the range of 60 to 95 percent, the steps comprising:

charging the photoconductive layer of said sheet material with a uniform electrostatic charge;

exposing said charged sheet material to a light pattern corresponding to the image to be reproduced to form on the photoconductive layer of said sheet material a latent electrostatic image corresponding to said image to be reproduced;

developing said latent image with a hydrophobic toner and then heat fixing said toner onto said photoconductive layer;

then wetting said photoconductive layer with a treating solution consisting essentially of an aqueous solution containing dissolved therein at least one acid selected from the group consisting of phosphoric acid and acetic acid, at least one phosphate selected from the group consisting of diammonium hydrogen phosphate and ammonium dihydrogen phosphate and at least one metal ion having a valence of at least 2, to make the non-imaged portion of said photoconductive layer hydrophilic while the imaged portion remains hydrophobic and to make said intermediate layer water-insoluble.

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96—1 R, 1.8, 33; 117—17.5, 218; 101—462, 465